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Polycyclic aromatic hydrocarbons in water and bottom sediments of the non-flow reservoir with recreational use

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ABSTRACT

The article presents the problem of contamination of non-flow anthropogenic reservoir with intensive recreational use with polycyclic aromatic hydrocarbons (PAHs) in the conditions of the small forest catchment. The seasonal and spatial variability of the tested substances was determined. In water, the total PAHs ranged from 0.0222 to 0.128 µg/L in spring, from 0.0853 to 1.35 µg/L in summer, from values below the quantification limit to 0.130 µg/L in autumn and from 0.0691 to 0.264 µg/L in winter. While, in sediments ranged from 49.0 µg/kg dry matter (DM) to 390 µg/kg DM in spring, from 77.6 to 272 µg/kg DM in summer, from 111 to 446 µg/kg DM in autumn and from 42.6 to 347 µg/kg DM in winter. There was no correlation between the concentration of total PAHs and selected water parameters, and strong linear relationships between the sum of PAHs and, individually, dry matter, mineral matter, and volatile matter of the sediments were observed. It was determined that PAHs in the sediments are potentially pyrogenic, and the concentrations of these compounds were below levels thought to be toxic to benthic organisms.

Keywords: Diagnostic ratios; Ecological risk; Non-flow reservoir; Polycyclic aromatic hydrocarbons; Seasonal and spatial variability

1. Introduction

The type and degree of pollution of anthropogenic lakes, taking into account, inter alia, the influence of catchment factors and human pressure is the subject of research all over the world. To a large extent, the source waters influence the water quality and bottom sediments of these lakes. The lack of river flowing into the reservoir (typical for anthropogenic lakes) creates unique conditions for determining the level of polycyclic aromatic hydrocarbons (PAHs) from other sources.

PAHs are widespread, persistent organic pollutants and known carcinogens with both natural and anthropogenic sources [1,2]. Natural sources of PAHs include forest fires, volcanic eruptions, natural oil leakage, diagenesis of organic matter and plant synthesis [2,3]. However, input from these sources is generally low compared with that from anthropogenic sources, which can be grouped into pyrogenic and petrogenic [4,5]. Pyrogenic sources include the combustion of fossil fuel and biomass, in turn petrogenic sources are associated with petroleum and slow maturation of organic matter [1,6–9]. PAHs derived from anthropogenic sources enter to the aquatic ecosystems through direct discharge, municipal or industrial effluents, run-off, dry and wet atmospheric deposition and air-water gaseous exchanges [2,7].

After entering the aquatic environment, PAHs are subject to sorption on particulate suspensions. After falling to the bottom, they accumulate in bottom sediments, where they can affect aquatic organisms, accumulate in them and become a sensitive indicator of anthropopression [10–12].

The levels of contaminants in the aquatic environment depend on many factors and may change seasonally, spatially or within various components of the environment,

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such as vegetation, fish, sediment, water and other aquatic resources [2]. There is ample evidence available to back up the statement that PAH emission rates and profiles change with the seasons. The weather conditions change seasonally, and the ambient temperature and sunlight are of great importance [13]. The seasonality of PAH changes may also be affected by air quality, which also change seasonally (inter alia, the influence of the heating season on air quality) [12].

To determine the potential sources of PAHs, diagnostic ratios are determined. They are based on the assumption that the ratio of selected PAHs is characteristic for a given emission source [3]. However, PAHs in the aquatic environment undergo photolysis [14], which may change the values of these indicators [13]. Despite this, many researchers use these ratios to assess the likely source of these substances in the aquatic environment [15–18].

The objective of this study was to characterize the type and the seasonal and spatial variability of PAHs in the non-flow Nakło–Chechło Reservoir located in the region of Upper Silesia (Poland), an area of high urban-industrial development. The study site is characterized by a small forest catchment, intensive recreational use and lack of river flowing. The potential sources of PAHs contamination in this reservoir have been identified. Moreover, the correlation between the selected physicochemical parameters of water and bottom sediments and the sum of PAHs was determined. Also, the influence of PAHs on benthic organisms in this reservoir was characterized based on ecotoxicological criteria.

2. Materials and methods

2.1. Study area

The study was conducted for the Nakło–Chechło Reservoir (Poland), located in the Upper Silesia – an area heavily transformed by human activity. The study area was a non-flow anthropogenic reservoir characterized by intensive recreational use. The reservoir has an area of 90.3 ha, the depth does not exceed 3.5 m. The reservoir's catchment area is approximately 1.3 km^2, of which 1.1 km^2 (84.6%) is covered by forests, and the remaining part by 0.2 km^2 (15.4%) by grasslands, bushes, roads, parking lots and developed areas [19].

Samples of water and bottom sediments from the Nakło–Chechło Reservoir were collected four times (representatively for each season) for 1 year, along the large axis of the reservoir. Water samples were collected at three points, from the surface (W1_S, W2_S, W3_S) and the bottom water layers (W1_B, W2_B, W3_B) in the water column at each point. Sediments were collected at five points from the upper layer (approximately 5 cm thickness of the sediment core) (S1, S2, S3, S4, S5) (Fig. 1). All samples were stored in a refrigerator at 4°C and analyzed no later than 72 h after collection.

2.2. Research methodology

Selected physicochemical parameters and PAHs concentration were determined in water and sediment samples. In order to determine the thermal-oxygen conditions in the reservoir, the oxygen concentration and temperature were measured at each season. The measurement was made by means of an Elmetron oxygen probe, at the deepest point of the reservoir (W3) at four different depths in the water column: 0.3 m – above the bottom and 1, 2 and 3 m respectively. In addition, chemical oxygen demand (COD), total carbon (TC) and total organic carbon (TOC) concentrations in water were determined. COD, TC and TOC measurements were determined for each water samples taken over 4 seasons (a total of 24 measurements). COD was determined by the spectrophotometric method using a CHZT Nanocolor 500D photometer. TC and TOC content in liquid samples were determined by means of infrared spectrometry using a Shimadzu TOC-5000 automatic carbon analyzer.

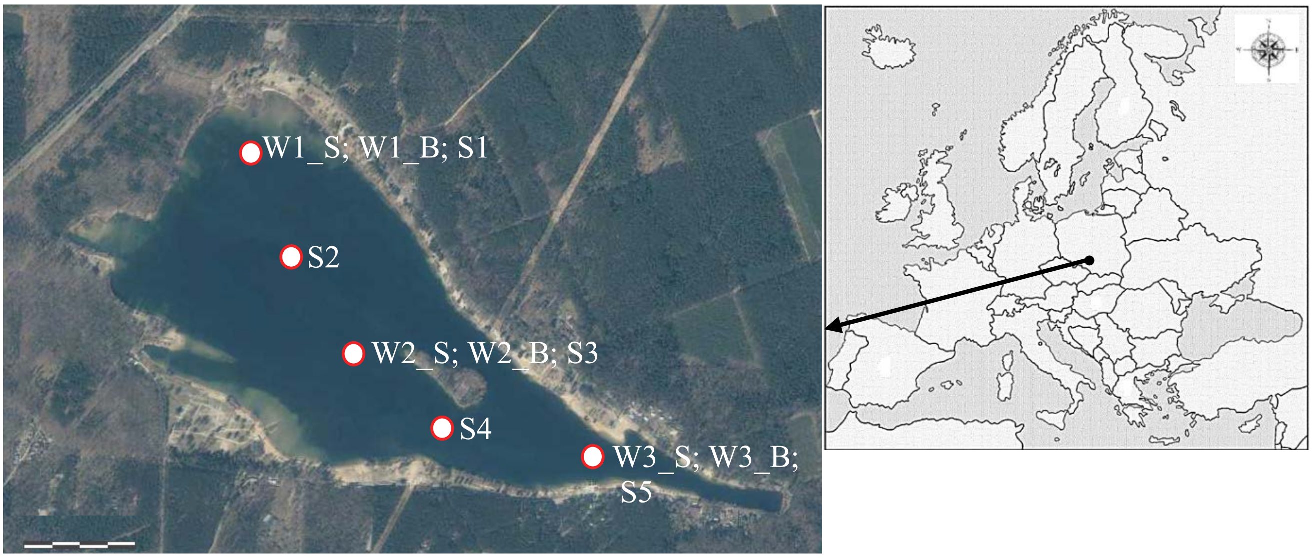
In the bottom sediments: dry matter (DM), mineral and volatile matter content (using the weight method) were determined. 20 measurements were made: for 5 sampling sites over 4 seasons. The obtained values of physicochemical parameters in water and sediments were used to determine the correlation between these values and the concentration of PAHs in the tested reservoir.

Samples preparation with some modification for PAHs analysis was performed according to the previously presented methodology [5] (Fig. 2). 1 L of water sample was three times extracted with dichloromethane (DCM) and cleaning on column with anhydrous sodium sulfate. After concentration to 1 mL the sample was analysis using a gas chromatograph coupled with mass spectrometry (GC-MS) with ZB-5MS column (30 m × 0.25 mm × 0.25 µm). Bottom sediments were sonicated (2 min × 30 min) with a mixture of dichloromethane: acetone (1v1). Then proceeded as with the water samples. Analysis of the obtained extracts were performed using a gas chromatograph with a flame ionization detector (GC-FID) with a ZB-50 column (30 m × 0.32 mm × 0.25 µm). In all samples the following compounds were determined: naphthalene (NP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP).

2.3. Quality assurance and quality control system

The quality assurance and quality control systems were used. The analyte solutions were prepared using dichloromethane and acetone (POCH Company, Poland). The certified PAHs standard (Sigma-Aldrich, United States) was used to prepare the stock standard solution. The stock deuterated standard solution and working calibration solutions were prepared by diluting. The calibration was done at five concentration levels. A standard solution derived from another series than calibration standard was used to check the calibration. The quality control of research was based on the analysis of blind samples and recovery with the working standard parallel for each series of samples. The obtained recovery values ranged from 90%–115% for the water samples and 70%–115% for the bottom sediment samples.

The limits of detection (LOD) were determined with the S/N = 3 method using consecutive dilution series.



Surface waters	Bottom sediments	Latitude	Longitude
W1_S, W1_B	S1	50°28’17.05” N	18°54’42.11” E
-	S2	50°28’09.08” N	18°54’45.66” E
W2_S, W2_B	S3	50°27’58.07” N	18°54’55.87” E
-	S4	50°27’52.66” N	18°55’11.63” E
W3_S, W3_B	S5	50°27’50.59” N	18°55’26.47” E

Fig. 1. Location of the study area and sampling sites in the Nakło–Chechło, Poland [20].

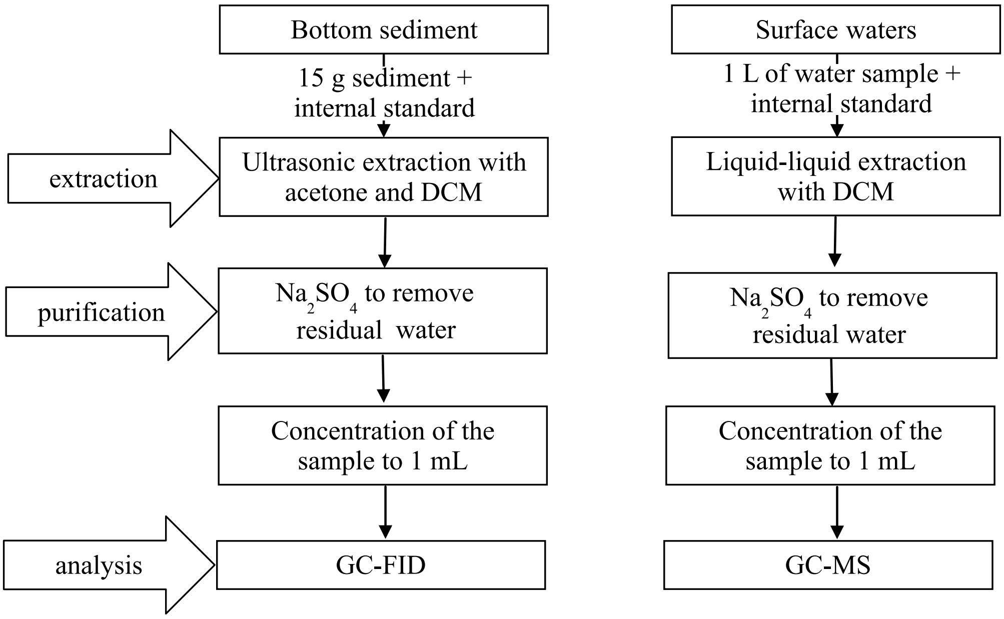


Fig. 2. Scheme of preparation of water and sediment samples.

The limits of quantification (LOQ) were defined as three times the LOD. The LOD was 0.00200 µg/L for BaP and 0.00300 µg/L for the others PAHs and the LOQ was 0.00600 µg/L for BaP and 0.00800 µg/L for the others PAHs in the water samples, respectively. While in the samples of bottom sediments the LOD and the LOQ were respectively 0.300 and 1.00 µg/kg calculated on the dry matter of the sediment.

3. Results and discussion

3.1. Water characterization

3.1.1. Seasonal variability

Mean concentrations of PAH sum in the water of the Nakło–Chechło Reservoir varied seasonally, with the lowest concentrations found in spring and autumn, and the highest in the summer. The sum of the analyzed PAHs ranged from 0.0222 to 0.128 μg/L (mean 0.0664 μg/L) in spring, from 0.0853 to 1.35 μg/L (mean 0.647 μg/L) in summer, from values below the quantification limit up to 0.130 μg/L (mean 0.0370 μg/L) in autumn and from 0.0691 to 0.264 μg/L (mean 0.191 μg/L) in winter (Table 1). The tested reservoir is a non-flow reservoir with a small forest catchment area, characterized by intensive recreational exploitation. Especially in summer, its increased use by tourists is observed, which in turn is associated with an increase in, among others, car traffic on the designated area. Surface runoff from these areas may be one of the likely sources of these pollutants at this time of the year.

The proportions of individual compounds in the total PAHs also changed seasonally. From spring to autumn, PAHs with two and three rings (LMW – low molecular weight) dominated, with a total average share of 85.3%. In winter, PAHs with a larger number of rings (HMW – high molecular weight) dominated, the average share of which was 80.3% (Fig. 3a). A higher share of PAHs with a higher molecular weight in waters in winter, compared to other seasons may indicate a different source of these compounds at this time of the year.

In turn, analyzing the share of individual PAHs in the water of the Nakło–Chechło Reservoir, it was found that it was varied throughout the research period. In spring dominated PHE (43.3%), ACE (15.0%), FL (14.3%) and NP (9.5%), in summer FL (29.5%), PHE (28.5%) and NP (11.4%), in autumn ACY (42.5%), NP (22.2%) and PHE (11.1%) in turn in winter PYR (35.5%), ANT (22.1%), BkF (12.1%) and BaP (8.8%) (Fig. 4a). The diversified distribution of PAHs in the water could be caused, on the one hand, by the movements of water masses under the influence of wind, and on the other hand, by the introduction of pollutants into the reservoir from various external sources, mainly with surface run-offs and deposition from the air.

3.1.2. Spatial variability

In the case of spatial variability, the range of the total PAHs at points W1 (reservoir depth at this point – 1.8 m) and W2 (reservoir depth – 2.2 m) was comparable. In turn, in the deepest point of the W3 reservoir (3.5 m), the mean concentrations of total PAHs were the highest (Fig. 3b). It can be assumed that as the depth of the reservoir increases, the concentration of total PAHs increases, which is indicated, on the role of reservoir morphometry in the allocation of these pollutants.

Comparing the obtained concentrations in the water column, after removing the extreme values, no significant differences were found between the sum of PAHs in the surface layer and in the bottom layer (Fig. 3c). The research object was a shallow reservoir with a maximum depth of about 3.5 m. Oxygen concentration and water temperature slightly differ in the water column in subsequent seasons (Table 2). The eumictic nature of the reservoir, mixability under the influence of wind and homothermia of water masses most probably contribute to the lack of differences in the concentrations of the tested compounds in the water column.

3.1.3. Correlation between the PAHs and physicochemical parameters

Apart from the determination of PAHs, other physicochemical parameters were also determined in the water samples (among others pH, redox, COD, forms of carbon). The correlation between the sum of PAHs and COD, TC and

Table 1
PAH concentration in the surface water of the Nakło–Chechło Reservoir (μg/L)

Compound	Spring (n = 6)		Summer (n = 6)		Autumn (n = 6)		Winter (n = 6)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
NP	0.000885	bdl-0.0258	0.130	bdl-0.308	0.0154	bdl-0.0514	–	bdl
ACY	0.00407	bdl-0.0105	0.0135	0.0104–0.0178	0.00279	bdl-0.0113	–	bdl
ACE	0.00333	bdl-0.0199	0.0489	bdl-0.135	–	bdl	0.00142	bdl-0.00849
FL	0.0132	bdl-0.0335	0.110	0.0227–0.206	0.00264	bdl-0.0158	–	bdl
PHE	0.0273	bdl-0.0429	0.256	bdl-0.626	0.0103	bdl-0.0530	–	bdl
ANT	–	bdl	–	bdl	–	bdl	0.0363	0.0118–0.132
FLA	–	bdl	0.0241	bdl-0.0543	–	bdl	–	bdl
PYR	0.00250	bdl-0.0150	0.00284	bdl-0.00886	0.00297	bdl-0.0102	0.0604	0.0286–0.0873
BaA	–	bdl	–	bdl	–	bdl	0.0138	bdl-0.0316
CHR	–	bdl	–	bdl	–	bdl	0.0125	bdl-0.0236
BbF	0.00297	bdl-0.0178	0.00485	bdl-0.0220	–	bdl	0.0149	bdl-0.0539
BkF	0.00427	bdl-0.0256	0.0141	0.00894–0.0182	–	bdl	0.0304	bdl-0.0633
BaP	–	bdl	0.00764	bdl-0.0269	0.00148	bdl-0.00890	0.0212	bdl-0.0647
IcdP	–	bdl	0.00447	bdl-0.0162	0.00141	bdl-0.00845	–	bdl
DahA	–	bdl	0.0140	bdl-0.0429	–	bdl	–	bdl
BghiP	–	bdl	0.0166	bdl-0.0701	–	bdl	–	bdl
∑PAHs	0.0664	0.0222–0.128	0.647	0.0853–1.35	0.0370	bdl-0.130	0.191	0.0691–0.264

bdl – data below quantitation limit

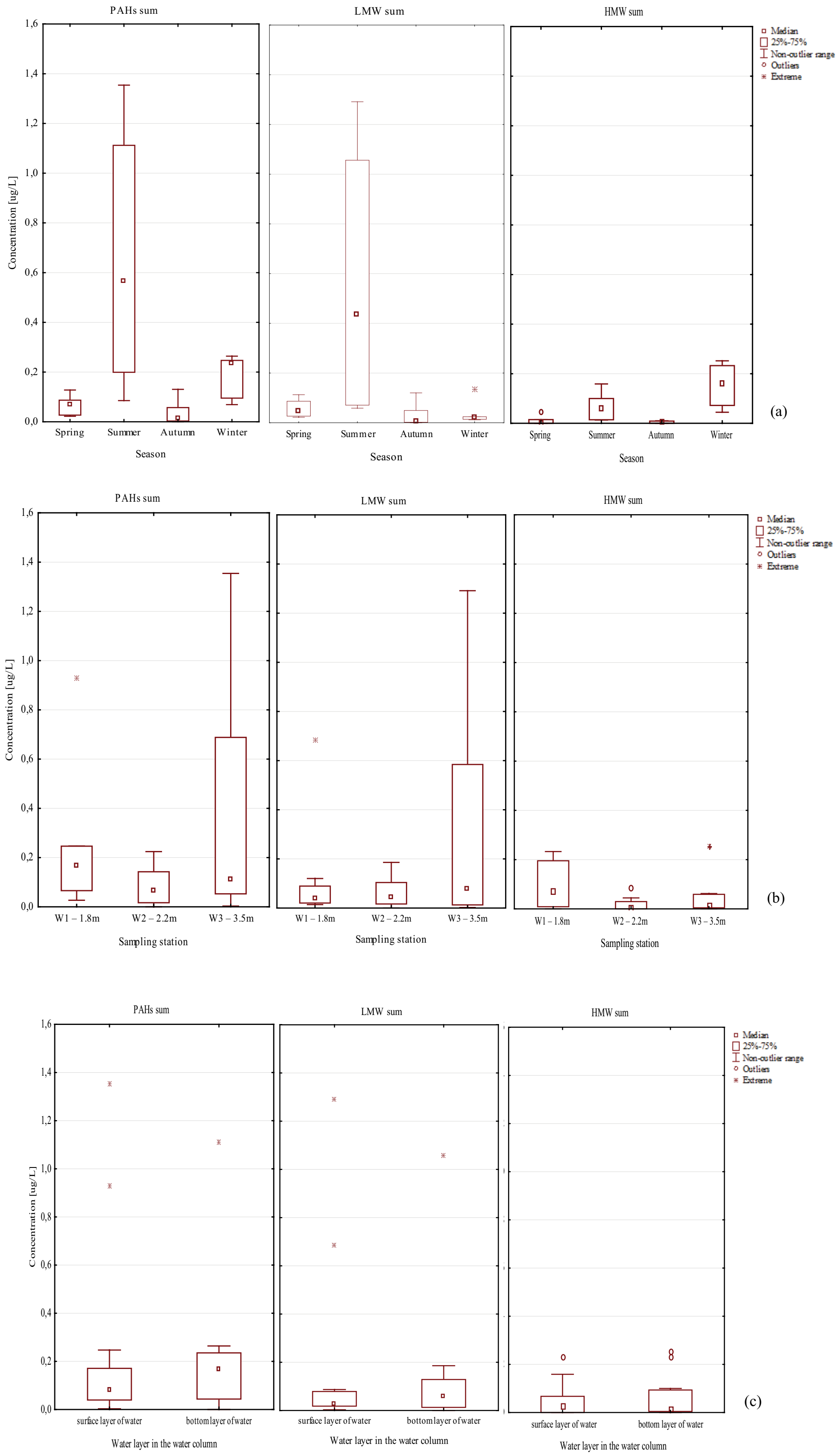


Fig. 3. Variability of the total PAHs in the water of the Nakło–Chechło Reservoir: (a) seasonal variability, (b) spatial variability depending on the sampling site, and (c) spatial variability in the water column.

TOC was determined in the water samples. The normality of the obtained data was first checked with the Shapiro–Wilk test. In the case of the parameters characterizing the water quality, it was found that the data were not normally distributed and the Spearman's rank correlation was used to determine the correlation. On the basis of the obtained values of the coefficient, it was found that there was no correlation between the concentration of total PAH and COD, TC and TOC in the water of the tested reservoir (Table 3).

3.2. Sediment characterization

3.2.1. Seasonal variability

The sum of the analyzed PAHs in the bottom sediments of the Nakło–Chechło Reservoir ranged from 49.0 to 390 µg/kg DM (average 227 µg/kg DM) in spring, from 77.6 to 272 µg/kg DM (average 147 µg/kg DM) in summer, from 111 to 446 µg/kg DM (average 267 µg/kg DM) in autumn and from 42.6 to 347 µg/kg DM (average 200 µg/kg DM) in winter (Table 4). In the case of bottom sediments, there were no such significant differences in the seasonal variability of PAHs as in the case of water samples. In contrast to the water samples, PAHs with higher molecular weight dominated in the bottom sediments (Fig. 5a). PAHs with low molecular weight are characterized by higher solubility in water compared to PAHs with high molecular weight [21]. The higher their weight is, the lower is their water solubility [13].

The percentage of individual PAHs was comparable throughout the entire study period. BaA (on average 19.5% – spring, 20.9% – summer, 14.2% – autumn, 28.5% – winter) and BghiP dominated (average 18.4% – spring, 15.1% – summer, 17.8% – autumn, 13.9% – winter). About 10% share in the total of all PAHs was found for FL, CHR, BbF and BaP (Fig. 4b).

3.2.2. Spatial variability

In the case of bottom sediments, no relationship was found between the sampling sites and the total PAHs in the bottom sediment. The distribution of pollutants in the bottom sediments of non-flow reservoirs may be influenced by their morphometry, including the shape of the bottom (bottom topography) (Fig. 5b).

3.2.3. Correlation between the PAHs and physicochemical parameters

In bottom sediment samples, apart from PAHs, the pH, redox, dry matter, mineral and volatile matter content were determined. Similarly as in the case of water samples, the first step was to examine the data distribution using the Shapiro–Wilk test. It was found that the data characterizing the quality of bottom sediments were normally distributed and the Pearson linear correlation was used to determine the correlation. The value of the correlation coefficient is in the closed interval [−1, 1] and the greater the absolute value of the coefficient, the stronger the linear relationship between data is. In the case of the analyzed variables, a strong linear relationship was found in each case (Table 3). It has been reported that the relationship between ∑PAHs and dry matter and volatile matter is inversely proportional (negative values of the correlation coefficient). While, the relationship between ∑PAHs and mineral matter is directly proportional. Many researchers, for example, Meyers and Qujnn [22], Keil et al. [23], Witt [24], Staniszewska et al. [25] also found strong correlation between the total concentration of PAHs and the organic matter content in sediment.

3.2.4. Potential PAH sources

Due to the hydrophobic properties of PAHs, which are mainly sorbed on suspended solids, the analysis of possible sources of PAHs was limited to bottom sediments. An attempt to determine the origin of PAHs in the non-flow reservoir, characterized by intensive recreational exploitation, is important and justified, because on the one hand, the lack of inflow to the reservoir excludes the introduction of these pollutants with the supply waters, which limits the sources to two main: surface runoff and

Table 2
Thermal-oxygen relations at the point W3 in the water column (range)

Parameter	Spring ($n = 4$)	Summer ($n = 4$)	Autumn ($n = 4$)	Winter ($n = 4$)
Temperature (°C)	21.3–22.3	23.6–23.8	16.2–16.3	11.0–11.1
Oxygen concentration (mgO_2/dm^3)	9.2–9.4	7.0–7.8	8.4	9.5–9.7

Table 3
Correlation describing the relationship between the total content of PAHs and water and sediment parameters

Spearman's rank order correlation, $n = 24$ for water samples		Pearson's linear correlation, $n = 20$ for sediment samples	
	∑PAHs (µg/L)		∑PAHs (µg/kg DM)
COD (mg/L)	0.0854	Dry matter (%)	–0.664
TC (mg/L)	–0.0248	Mineral matter (%)	0.637
TOC (mg/L)	–0.221	Volatile matter (%)	–0.669

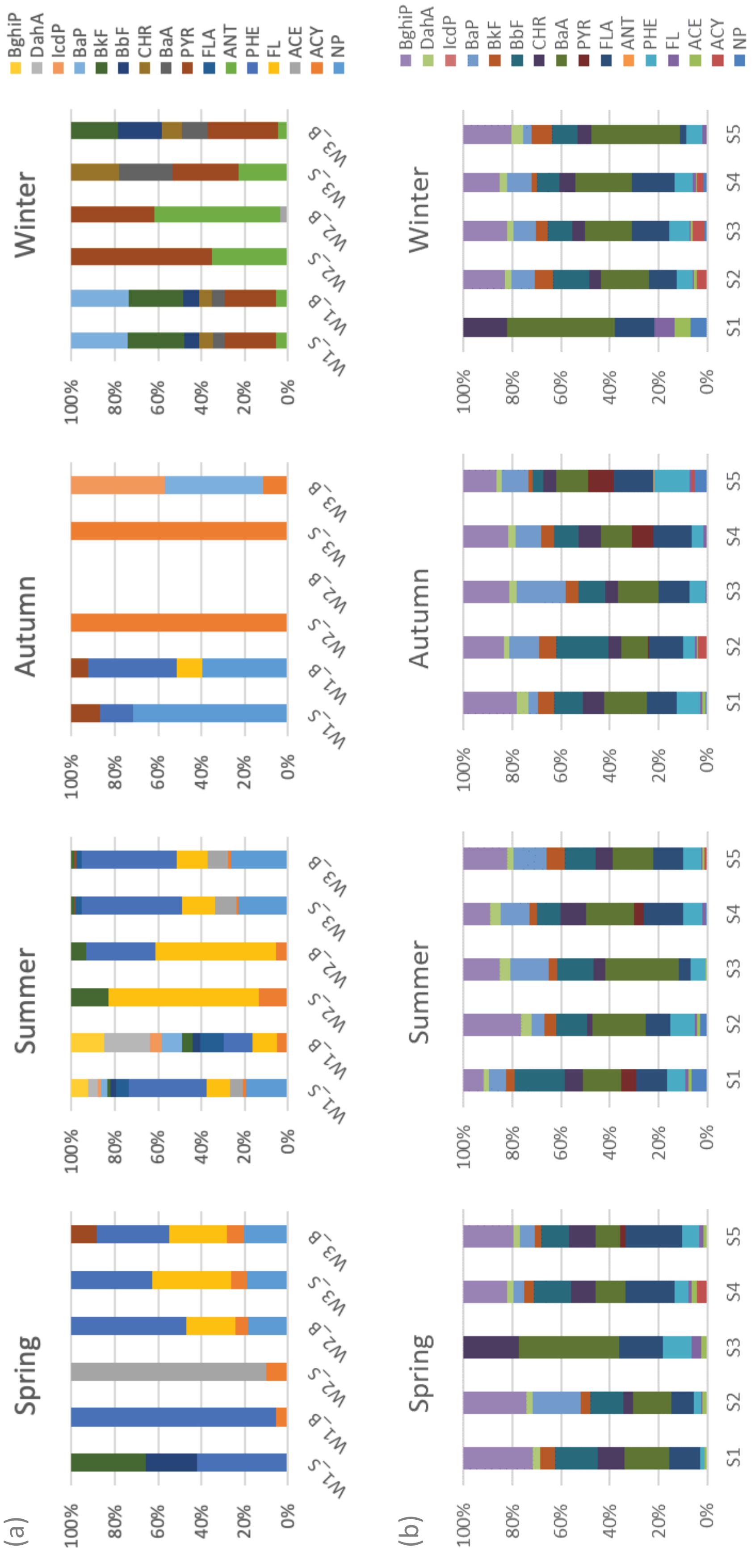


Fig. 4. Percentage of selected PAHs in (a) water and (b) bottom sediments.

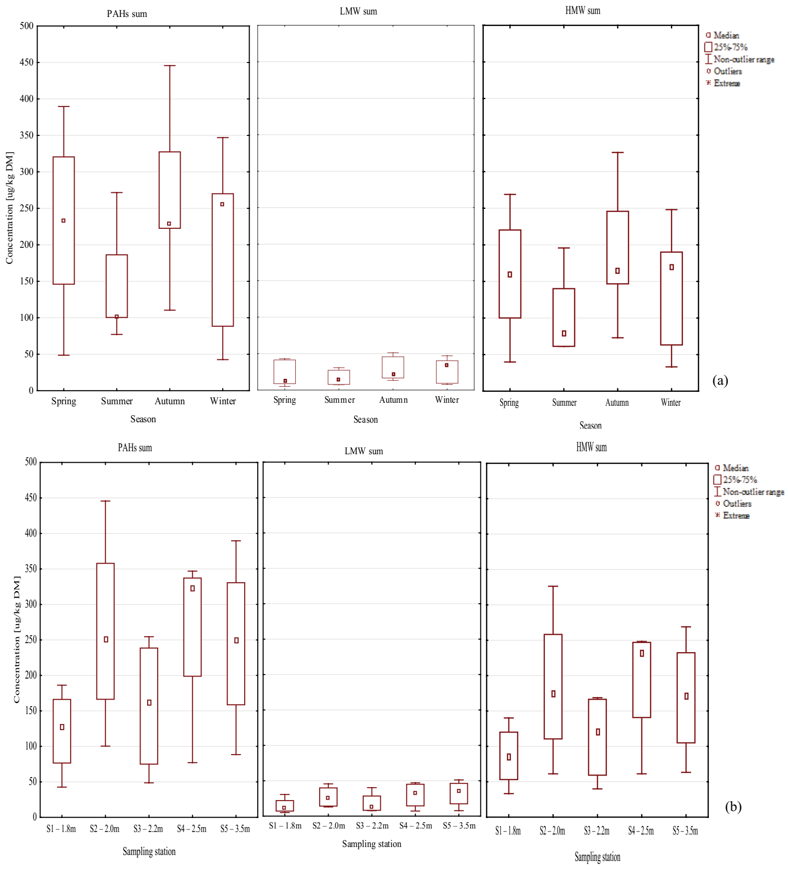


Fig. 5. Variability of the total PAHs in the bottom sediment of the Nakło–Chechło Reservoir: (a) seasonal variability and (b) spatial variability

Table 4
PAH concentration in bottom sediments of the Nakło–Chechło Reservoir (µg/kg DM)

Compound	Spring (n = 5)		Summer (n = 5)		Autumn (n = 5)		Winter (n = 5)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
NP	0.288	bld-1.44	3.22	bld-12.1	3.04	bld-12.0	2.56	bld-5.43
ACY	2.88	bld-13.2	0.782	bld-3.91	3.68	bld-15.6	6.56	bld-12.7
ACE	3.79	1.20–5.99	1.18	bld-2.28	0.933	bdl-2.65	1.77	bdl-2.81
FL	3.04	bdl-6.88	1.10	bdl-2.46	2.45	1.20–3.98	2.34	1.12–4.33
PHE	12.2	2.62–28.5	11.4	5.97–20.7	19.4	10.5–33.0	14.4	bld-26.6
ANT	–	bld	–	bld	0.226	bld-1.13	–	bld
FLA	40.5	8.64–89.1	16.9	4.51–33.0	38.0	14.0–60.7	27.8	2.42–60.6
PYR	1.73	bld-8.65	2.82	bld-11.0	11.3	bld-29.2	–	bld
BaA	32.4	20.1–39.6	28.6	15.2–46.0	35.4	19.2–49.1	46.5	18.9–79.8
CHR	22.2	8.97–42.0	9.52	2.26–18.1	17.6	9.90–30.1	12.6	4.87–23.8
BbF	30.2	bld-48.3	21.5	7.59–38.1	34.5	9.66–94.2	21.4	bld-40.8
BkF	7.93	bld-12.9	7.65	2.41–20.8	14.3	3.55–31.7	9.29	bld-20.1
BaP	16.9	bld-45.8	15.9	5.32–35.9	32.9	4.55–54.1	17.5	bld-35.6
IcdP	–	bld	–	bld	–	bld	–	bld
DahA	5.94	bld-10.8	4.56	3.17–7.42	7.19	4.58–10.4	5.58	bld-9.43
BghiP	47.4	bld-79.3	22.3	8.56–48.6	46.1	24.1–73.8	32.0	bld-51.7
∑PAHs	227	49.0–390	147	77.6–272	267	111–446	200	42.6–347

bdl – data below quantitation limit

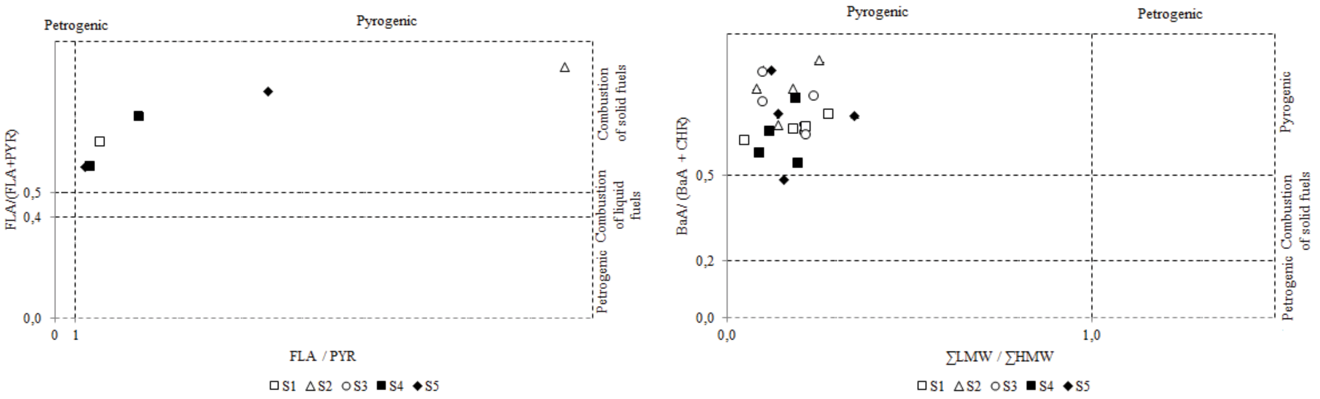


Fig. 6. Selected diagnostic ratios of PAHs in sediments.

air deposition. On the other hand, determining the potential sources of PAHs for places used for tourism, may contribute to the implementation of measures that may minimize the introduction of these pollutants into the aquatic environment.

The distinction between PAHs with low and high molecular weight can be used to identify a potential source of these pollutants in the ecosystem. Compared to the PAHs with a low molecular weight (two or three rings) imply petroleum pollution, those with a high molecular weight (more than four rings) come from fossil fuels combustion at a high temperature [26,27]. Moreover LMW PAHs are generally related with the high and acute toxicity of PAHs, while HMW PAHs are responsible for carcinogenicity, mutagenicity, and teratogenicity [28]. In turn, based on the ratio of ∑LMW/∑HMW, sources of PAH can be divided into pyrogenic (values below 1) and petrogenic (value above 1). The predominance of HMW PAHs and the ∑LMW/∑HMW value at the level of 0.1–0.3 suggested that PAHs in the sediments might derive primarily from pyrogenic origins. Other indicators determining the source of PAHs origin taking into account other HMW PAHs (FLA/PYR, FLA/(FLA + PYR), BaA/(BaA + CHR), BaP/BghiP) also indicate pyrogenic origin, including combustion of solid fuels, as likely sources of these compounds in sediments (Fig. 6).

3.2.5. Assessing the bottom sediment quality

Sediment pollution of the Nakło–Chechło Reservoir was assessed using the TEC (threshold effect concentration) and PEC (probable effect concentration) ecotoxicological criteria. TEC determines the concentration of PAHs below which no toxic effects on organisms are observed (I); PEC determines concentrations above which toxic effects on organisms are often observed (III). While the concentrations between the TEC and PEC values is considered as cause sporadic adverse effects (II) [29–31].

PAH concentrations in the bottom sediment of the Nakło–Chechło Reservoir in most cases do not exceed the TEC values (Table 5). Sporadic PAH concentration values between TEC and PEC were recorded only for acenaphthylene at S2, S3, S4. Therefore, it can be concluded that in the studied aquatic ecosystem there is no toxic effect of these compounds on benthic organisms.

Table 5
Classification of bottom sediments of the Nakło–Chechło based on ecotoxicological criteria

Compound	Literature values (µg/kg DM)[a]		Ecotoxicological classification				
	TEC	PEC	S1	S2	S3	S4	S5
			LMW PAHs				
NP	176	561	I	I	I	I	I
ACY	5.9	128	I	I/II	I/II	I/II	I
ACE	6.7	89	I	I	I	I	I
FL	77.4	536	I	I	I	I	I
PHE	204	1,170	I	I	I	I	I
ANT	57.2	845	I	I	I	I	I
			HMW PAHs				
FLA	423	2,230	I	I	I	I	I
PYR	195	1,520	I	I	I	I	I
BaA	108	1,050	I	I	I	I	I
CHR	166	1,290	I	I	I	I	I
BbF	240	13,400	I	I	I	I	I
BkF	240	13,400	I	I	I	I	I
BaP	150	1,450	I	I	I	I	I
IcdP	200	3,200	I	I	I	I	I
DahA	33	135	I	I	I	I	I
BghiP	170	3,200	I	I	I	I	I
			Total PAHs				
∑PAHs	1,610	22,800	I	I	I	I	I

[a] [29,30]

4. Conclusion

The type and degree of pollution of lakes and artificial water reservoir is the subject of research all over the world. The observed relatively high levels of pollution are related to, among others, with their introduction into reservoirs along with supply waters. Repeatedly, these reservoirs often act as the final absorber of various pollutants, where the effect of dilution on pollutants is usually not significant due to the low water exchange. The relatively high levels of pollutants are additionally affected by the persistent nature of some of them, as is in the case of PAHs. In the absence of typical for anthropogenic lakes river flow, the sources of the tested compounds are limited.

The conducted studies provided comparative material for the problem of contamination of non-flow anthropogenic reservoirs with PAH compounds in the conditions of the vestigial direct catchment (small forest catchment). Seasonal variability of PAHs in the water of the Nakło–Chechło Reservoir (increase of the concentration in summer), indicates the way of exploitation of the reservoir, in particular intensive recreational use, as one of the possible indirect causes of this condition. The spatial variability of PAHs indicates the role of reservoir morphometry in the allocation of these pollutants. The concentration of total PAHs in the water increased with increasing depth of the reservoir. While, in the case of bottom sediments, the topography of the reservoir bottom could have influenced the distribution of these compounds and no relationship between the sampling station and the sum of PAHs in the bottom sediment was found. In the case of spatial variability in the water column, no significant differences were found in the concentrations of PAHs between the surface and the bottom layer of water. This is due to the eumictic nature of the reservoir, susceptible to miscibility under the influence of wind and the homothermia of water masses. On the basis of the determined correlation coefficients, no correlation was found between the concentration of total PAHs and COD, TC and TOC in water. A strong linear relationship between the sum of PAHs and, individually, dry matter, mineral matter, and volatile matter of the sediments of the studied reservoir were observed.

The analysis of diagnostic ratios for bottom sediments shows that their values are similar to the values of indicators determining air quality for pyrogenic origins, including combustion of solid fuels as the likely source of these compounds in bottom sediments of the Nakło–Chechło Reservoir. In addition, a different distribution of PAHs in waters in the period from spring to autumn, compared to winter, may indicate their different sources in this period. A higher share of HMW WWA in winter indicates the deposition of air pollutants (combustion of solid fuels).

The quality of bottom sediments was assessed on the basis of PEC and TEC ecotoxicological indicators. The concentrations of PAHs in sediments in the Nakło–Chechło Reservoir were below levels thought to be toxic to benthic organisms.

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